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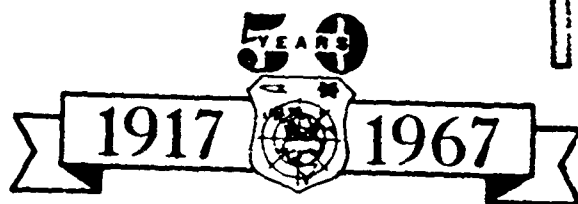


THE EFFECT OF SOME ADDITIVES ON THE THERMAL  
DECOMPOSITION OF AMMONIUM PERCHLORATE

by

A. A. Shidlovskiy, L. F. Shmagin,  
and V. V. Bulancev

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# EDITED MACHINE TRANSLATION

THE EFFECT OF SOME ADDITIVES ON THE THERMAL  
DECOMPOSITION OF AMMONIUM PERCHLORATE

By: A. A. Shidlovskiy, L. F. Shmagin, and  
V. V. Bulanov

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**ABSTRACT:** The purpose of this work was to investigate the thermal decomposition of ammonium perchlorate (AP) in the presence of oxides, chlorides, carbonates, and oxalates of certain metals. The decomposition was studied gravimetrically, at atmospheric pressure and 214-470C. The following values for activation energies were found: for the orthorhombic form, E = 40 kcal/mole; for the cubic form, E = 36-39 kcal/mole. Compounds of manganese and cobalt promote complete decomposition of AP at T < 240C. Compounds of iron, nickel, and chromium promote complete decomposition of AP at 270-280C. The rate of decomposition of AP is increased by the addition of compounds of copper, manganese, cobalt, as well as zinc oxide; it is retarded by the addition of compounds of iron, bivalent nickel, chromium, and vanadium pentoxide. For the same element, the activity of the compounds added decreases in the following order: Carbonate (oxalate), oxide, chloride.

Orig. art. has: 3 tables and 3 figures. English translation: 8 pages.

# U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

\* ye initially, after vowels, and after ъ, Ъ; e elsewhere.  
When written as ѣ in Russian, transliterate as yě or ě.  
The use of diacritical marks is preferred, but such marks  
may be omitted when expediency dictates.

THE EFFECT OF SOME ADDITIVES ON THE THERMAL  
DECOMPOSITION OF AMMONIUM PERCHLORATE

(Moscow Institute of Chemical Machine Building)

A. A. Shidlovskiy, L. F. Shmagin,  
and V. V. Bulanov

Many works have been dedicated to the thermal decomposition of pure ammonium perchlorate [AP] ( $\text{HIA}$ ) and of ammonium perchlorate with different additives. Kinetics of decomposition has been basically studied by measuring pressure or volume of liberated gases.

Bircumshaw and Newman [1] investigated decomposition of AP at 215-275°C. They found that decomposition of AP starts at the surface and spreads in the form of hemispheres, which then unite into a solid front. The process stops after decomposition of about 30% of the salt. The residue is a friable powder which is identical with the initial AP. Activation energy of decomposition of AP is  $E = 27.8$  for the orthorhombic and  $E = 18.9$  kcal/mole ( $1 \text{ kcal} = 4.1868 \text{ kJ}$ ) for the cubic form.

Galwey and Jacobs [2] studied decomposition of AP by the manometric method and found  $E = 24.6$  kcal/mole for the orthorhombic and cubic forms of AP. They confirmed the indication [1] that at a temperature higher than 300°C AP decomposes completely. Galwey and Jacobs [3] found  $E = 17.5$  for decomposition of AP and  $E = 30$  kcal/mole for decomposition of the residue from the low-temperature reaction at a temperature higher than 350°C. Measuring the dependence of ignition delay time on temperature, they found  $E = 41.1$  kcal/mole [4].

Rayevskiy and Manelis [5], using microfilm to measure the speed of growth of nuclei of decomposition of AP, found  $E = 31-33$  kcal/mole. Sung Ts'van-tsai [6] studied decomposition of AP by the manometric method and obtained an  $E$  of about 30 kcal/mole using different methods of calculation. According to data of Osada and Sakamoto [7], activation energy of decomposition of AP depends on dimension of particles. Activation energy of thermal decomposition of AP with metal oxide additives, according to source material, is about 30 kcal/mole and depends little on the chemical nature of the oxide.

Decomposition of AP was studied with the oxide additives,  $\text{MnO}_2$  [8, 15, 20],  $\text{Cu}_2\text{O}$  [10, 11, 20],  $\text{CuO}$  [9, 20],  $\text{ZnO}$  [12, 20],  $\text{Fe}_2\text{O}_3$  [13],  $\text{MgO}$  [14, 15],  $\text{Cr}_2\text{O}_3$  [15, 20],  $\text{Ni}_2\text{O}_3$ ,  $\text{Co}_2\text{O}_3$  +  $\text{Co}_3\text{O}_4$  [15], and also metal chlorides [7]. The action of catalytic additives is explained by their participation in the process of transmission of electrons from  $\text{ClO}_4^-$  to  $\text{NH}_4^+$ .

The purpose of our work was to study the thermal decomposition of AP in the pure state and in presence of oxides, chlorides, carbonates and oxalates of certain metals.

### Experimental Part

The kinetics of thermal decomposition was studied gravimetrically. Decomposition was conducted in an atmosphere of air at atmospheric pressure. Free separation of products of decomposition prevented them from influencing the decomposition of the AP [6]. A sample of the substance (about 150 mg) was placed in a small glass cup, which, with the help of a glass capillary, was lowered into a furnace which was preliminarily heated to a given temperature and was suspended on the arm of torsion scales [BT-200] (BT-200) (accuracy of weighing is 0.2 mg). Temperature in the furnace was regulated with a precision of  $\pm 1^\circ\text{C}$ .

AP recrystallized from water was dried at  $100-110^\circ\text{C}$ , crushed, and sifted through an 018 sieve. In all experiments we used a single sample of AP; the sample was stored in an exsiccator over anhydrous calcium chloride.

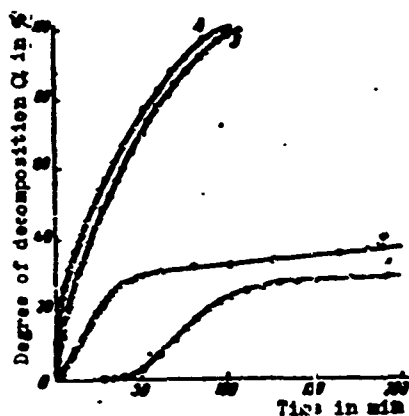


Fig. 1. Decomposition curves of ammonium perchlorate.  
Temperature, in  $^\circ\text{C}$ :  
1 - 230, 2 - 281,  
3 - 410, 4 - 410 (residue from low-temperature reaction):

Kinetics of decomposition of pure AP was studied in the  $214-470^\circ\text{C}$  temperature range. Figure 1 shows curves of decomposition  $\alpha-t$  (degree of decomposition - time) of pure AP and a curve of decomposition at  $410^\circ\text{C}$  of the residue from the low-temperature reaction (at  $230^\circ\text{C}$ ). Decomposition of the orthorhombic form of AP ( $t < 240^\circ\text{C}$ ) is characterized by the presence of an induction period, a period of acceleration, and a period of decomposition, which corresponds to the formation, growth and accretion of centers of decomposition into a solid front [1]. Decomposition ceases after  $\alpha \approx 30\%$ , is reached after which there remains a white, porous, slightly baked residue of AP. Maximum speed of decomposition is developed when  $\alpha$  is about 10%.

Decomposition of the cubic form of AP ( $240-300^\circ\text{C}$ ) takes place without an induction period. Speed of decomposition reaches a

maximum at  $\alpha = 3-5\%$ . It is possible to distinguish three periods on the decomposition curve: a period of acceleration, a period of rapid decomposition, and a period with a considerably lower, almost constant rate of decomposition. Transition to slow decomposition occurs at  $\alpha = 20-30\%$ , where the higher the decomposition temperature, the higher the  $\alpha$  at which this transition occurs.

At 300-380°C, the reproducibility of kinetic curves is poor due to change of the mechanism of AP decomposition [3]. At a temperature higher than 380°C, the rate of AP decomposition decreases with time. Decomposition is complete.

Decomposition was studied of the residue from low-temperature reaction (at 230°C). For this the residue was transferred to another furnace after the reaction was over, and its decomposition was studied. The decomposition curves of the residue are reproduced at temperatures higher than 380°C. Decomposition is complete. The maximum rate of decomposition of residue is higher than for initial AP. The residue from the low-temperature reaction burns 1-2 minutes after thrusting the sample into a furnace heated to 450°C, while initial AP bursts into flames at 470°C. At a temperature above 300°C, a noticeable sublimation of AP was observed.

A kinetic analysis of decomposition curves was made with the help of the equation of Yerofeev [16]:

$$-\ln(1-\alpha) = kt^n \quad (1)$$

where  $\alpha$  is the degree of decomposition up to the moment of time  $t$ ;  $k$  is a constant. Values of  $k$  and  $n$  were determined from graphs of  $\lg [-\lg(1-\alpha)] - \lg t$ . Values of the constant  $k$  obtained from these graphs were recalculated using the equation of Sakovich [16]:

$$K = nk \cdot t^n \quad (2)$$

where  $K$  is the rate constant with the dimensionality of the monomolecular reaction rate constant ( $t^{-1}$ ),  $k$  is the constant from the equation of Yerofeev.

Table 1. Kinetic Characteristics of Thermal Decomposition of Ammonium Perchlorate

Decomposition temperature in °C	Limits of applicability of Yerofeev equation, $\alpha$ % (from-to)	Exponent, $n$	Pre-exponential factor, $C$	Activation energy, $E$ in kcal/mole
214-236	0-12	4.5	$1.6 \cdot 10^{10}$	40.1
250-300	0-20	1.2	$1.3 \cdot 10^8$	25.1
400-470	10-50	0.8	$2.0 \cdot 10^7$	28.3
	80-90	1.1	$1.1 \cdot 10^8$	23.7
320-450 <sup>1</sup>	0-40	0.6	$4.5 \cdot 10^{10}$	38.1
	40-80	1.8	$5.9 \cdot 10^8$	25.3

<sup>1</sup>Residue from low-temperature reaction.

The limits of applicability of the Yerofeev equation are given in Table 1. The straight lines  $[\lg - \lg(1 - \alpha)] - \lg t$ , corresponding to decomposition of AP and of the residue from the low-temperature reaction at a temperature higher than  $380^{\circ}\text{C}$ , have a break at  $\alpha = 40-50\%$ . Here different values  $n$  and  $k$  are obtained for the beginning and for the end of decomposition.

Activation energy values were determined from graphs  $\lg K = \frac{1}{T}$  (Fig. 2). From Fig. 2 it is clear that phase transition at  $240^{\circ}$  change of decomposition mechanism at  $300-380^{\circ}$  [3] cause a sharp decrease in the rate constant. Thus the value of maximum decomposition rate of AP sharply changes at these temperatures. The value  $n = 4.5$  obtained for the orthorhombic form corresponds to the value in work [2]. During decomposition of the cubic form of AP the exponent is close to one and even less than one, i.e., the reaction becomes monomolecular and passes into the diffusion region [16].

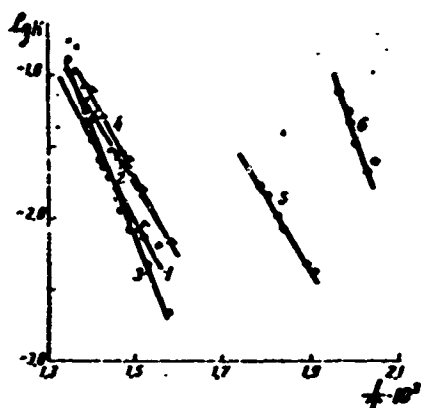


Fig. 2. Dependence of  $\lg K$  on  $1/T$  during decomposition of ammonium perchlorate.  
 1 -  $t > 380^{\circ}\text{C}$ ,  $\alpha < 50\%$ ;  
 2 -  $t > 380^{\circ}\text{C}$ ,  $\alpha > 50\%$ ;  
 3 - residue from low-temperature reaction,  $t > 380^{\circ}\text{C}$ ,  $\alpha < 40\%$ ;  
 4 - residue from low-temperature reaction,  $t > 380^{\circ}\text{C}$ ,  $\alpha = 40-80\%$ ;  
 5 -  $t = 240-300^{\circ}\text{C}$ ;  
 6 -  $t = 214-236^{\circ}\text{C}$ .

The value of activation energy obtained by us for the orthorhombic form of AP is somewhat higher than that in works [1-3]; this can be explained by the fact that during AP decomposition in a closed volume side reactions which influence decomposition can occur. In our experiments, separation of products of decomposition was free. The value of activation energy for the decomposition of the residue from the low-temperature reaction at  $t > 380^{\circ}$  is close to the  $E$ , obtained in work [4] during the study of ignition delay time. Decomposition of initial AP at this temperature takes place with a considerably smaller  $E$ , which may be connected with the influence of intercrystalline material.

#### Thermal Decomposition of AP with Additives

The additives used during thermal decomposition of AP were basically compounds (oxides, chlorides, carbonates, and oxalates) of the d-elements of the fourth period of D. I. Mendeleev's periodic system (from V to Zn) in the form of standard preparations ("analytically pure" or "pure") or preparations synthesized [17, 18, 19]. The additives were crushed and sifted through an 018 sieve. The content of the additive was most frequently 5% in weight: such a large quantity of additive was taken in order to clearly reveal the character of its influence. Mixtures were prepared by mechanical mixing of additive samples and AP (we used the same AP sample as was used during decomposition of pure AP. Prepared mixtures were stored in an exsiccator over anhydrous calcium chloride.

Table 2 gives data on the influence of metallic oxides on the thermal decomposition of AP.

Table 2. Kinetic Characteristics of Thermal Decomposition of Ammonium Perchlorate in the Presence of Metallic Oxides

Additive (5%)	Temperature limits, °C	Exponent, n	Activation energy, E, kcal/mole	Pre-exponential factor, C
MnO <sub>2</sub> (according to Frem. [17])	208-229	1.6	48.2	2.4·10 <sup>11</sup>
MnO <sub>2</sub> (pyrolusite)	214-245	1.4	33.7	5.0·10 <sup>11</sup>
Co <sub>2</sub> O <sub>3</sub>	214-245	1.4	38.3	7.4·10 <sup>11</sup>
CuO	239-270	2.2	53.5	5.0·10 <sup>12</sup>
Cu <sub>2</sub> O	250-270	1.6	45.5	1.4·10 <sup>11</sup>
Fe <sub>2</sub> O <sub>3</sub>	250-296	1.2	41.0	2.6·10 <sup>11</sup>
NiO	270-296	1.2	49.2	6.3·10 <sup>11</sup>
V <sub>2</sub> O <sub>5</sub>	250-303	1.2	43.7	1.6·10 <sup>15</sup>
Cr <sub>2</sub> O <sub>3</sub>	260-309	1.1	30.1	8.0·10 <sup>11</sup>

<sup>1</sup>At a temperature higher than the upper limit the mixtures ignited in the furnace.

From Table 2 it is clear that the action of the additive depends on the chemical nature of the oxide. In Fig. 3 there are curves of decomposition of AP in the presence of certain oxides.

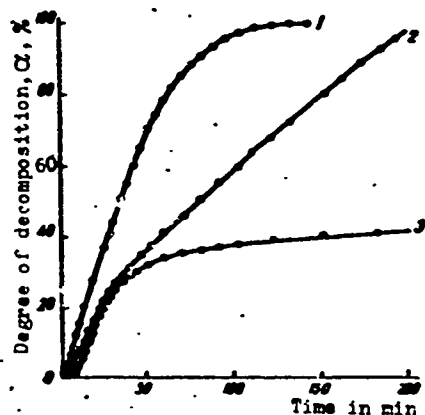


Fig. 3. Decomposition curves of ammonium perchlorate in the presence of 5 wt % of oxides. 1 - MnO<sub>2</sub> (according to Frem) 224°C; 2 - NiO, 280°C; 3 - CuO, 260°C.

Decomposition of AP is influenced most by the presence of compounds of manganese (MnO<sub>2</sub>, MnCO<sub>3</sub>, MnCl<sub>2</sub>·4H<sub>2</sub>O) and cobalt (Co<sub>2</sub>O<sub>3</sub>, CoCO<sub>3</sub>, CoC<sub>2</sub>O<sub>4</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O). In the presence of these additives AP is decomposed completely even at 210-220°. The induction period is absent in a majority of cases. The decomposition rate of AP is sharply increased. The maximum rate of decomposition of AP varies practically in proportion to the content of the additive, within limits of 1-5%.

In the presence of copper compounds (Fig. 3) maximum rate of decomposition increases. Degree of decomposition is increased insignificantly (Fig. 3). Curves of AP decomposition do not change their character in the presence of copper compounds. The induction period is shortened at a temperature below 240°. Mixtures of AP with 5% CuCO<sub>3</sub>, Cu<sub>2</sub>O, CuO, Cu<sub>2</sub>Cl<sub>2</sub> and CuCl<sub>2</sub>·2H<sub>2</sub>O begin to burn at a furnace temperature of 265°, 275°, 280°, 285° and 287°C, respectively. After burning out

of mixtures there remains on the cup a greenish deposit which is soluble in water with the formation of a bluish solution, i.e.,  $\text{CuCl}_2$  is formed. During a change within limits of 1-5% of content of copper compounds, their influence on AP decomposition does not change.

Compounds of iron ( $\text{Fe}_2\text{O}_3$ ,  $\text{FeC}_2\text{O}_4$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), nickel ( $\text{NiO}$ ,  $\text{NiC}_2\text{O}_4$ ,  $\text{NiCO}_3 \cdot \text{Ni}(\text{OH})_2$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), chromium ( $\text{Cr}_2\text{O}_3$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) and vanadium ( $\text{V}_2\text{O}_5$ ) affect AP decomposition at temperatures above  $240^\circ\text{C}$ .

Here the maximum rate of decomposition of AP decreases, and the rate of decomposition in the third, the slowest, period increases (Fig. 3). At  $270$ - $280^\circ$  AP is decomposed completely with these additives. Rate of decomposition in the third period is proportional within limits of 1-5% to the amount of additive. Maximum rate decreases with decrease to a certain limit of the quantity of these additives. For compounds of iron and nickel (II), this limit is about 2.5%; for compounds of chromium and vanadium it is less than 1%. With a further decrease in the quantity of additive the maximum rate increases and approaches maximum rate of decomposition of pure AP.  $\text{MgO}$  and  $\text{ZnO}$  interact chemically with AP when heated. Here a liquid phase is formed, which apparently explains the influence of these additives on the decomposition of AP.

It is necessary to note that introduction of a majority of the additives investigated greatly lowers the temperature at which AP ignites.

Table 3 gives data about the thermal decomposition of AP in the presence of different cobalt compounds.

Table 3. Kinetic Characteristics of Ammonium Perchlorate Decomposition in the Presence of Cobalt Compounds

Additive (5%)	Temperature limits, $^\circ\text{C}$	Exponent, n	Activation energy, E in kcal/mole	Pre-exponential factor, C
$\text{CoCO}_3$	208-224	1.4	46.7	$1.4 \cdot 10^{10}$
$\text{CoC}_2\text{O}_4$	210-229	1.7	43.7	$5.4 \cdot 10^{10}$
$\text{Co}_2\text{O}_3$	214-245	1.4	38.3	$7.4 \cdot 10^{11}$
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	214-250	1.1	36.0	$6.3 \cdot 10^{12}$

<sup>1</sup>At a temperature higher than the upper limit, the mixtures ignited in the furnace.

From Table 3 it is clear that the effect of additives depends on the nature of the chemical compound of the given element. The activity of an additive decreases in this order: carbonates (oxalates) - oxides - chlorides. In the process of thermal decomposition of AP all additives which we investigated were turned into, the most characteristic oxides for the given metal. The activity of the additive, apparently, is determined by the ease with which it can be

transformed into an oxide and by the properties of the oxide formed.

### Conclusions

1. The thermal decomposition of ammonium perchlorate was studied gravimetrically at atmospheric pressure and 214-470°C. The following values of activation energies of decomposition were found: for the orthorhombic form,  $E = 40$  kcal/mole; for the cubic form,  $E = 24-28$  and for the residue from the low-temperature reaction,  $E = 36-39$  kcal/mole.

2. The influence of oxides, chlorides, carbonates and oxalates of a number of metals on thermal decomposition of ammonium perchlorate was studied. It was shown that compounds of manganese and cobalt promote complete decomposition of ammonium perchlorate at temperatures below 240°C. Compounds of iron, nickel, and chromium promote complete decomposition of AP at 270-280°C.

3. At the same temperature the maximum rate of decomposition of ammonium perchlorate with additives of Cu, Mn, Co, compounds and also with ZnO is greater than the maximum rate of decomposition of pure ammonium perchlorate; the maximum rate of decomposition of mixtures of AP with compounds of iron, nickel (II), chromium, and also with  $V_2O_5$  is lower than for pure ammonium perchlorate.

4. The activity of additives of the same element decreases in this order: carbonate (oxalate) - oxide - chloride.

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